

the technique gives excellent qualitative agreement with compositions determined with an amino acid autoanalyzer.

The simplicity and low cost of this technique commend its use for instructional, as well as research purposes.

Acknowledgement

This work was supported, in part, by a grant from the Graduate School of The Ohio State University.

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First received December 6th, 1965

Modified December 27th, 1965

J. Chromatog., 23 (1966) 309-312

Purification of polycyclic hydrocarbons by chromatographic decomposition of their picrates, trinitrobenzolates and styphnates

The secondary reactions caused in adsorption chromatography on alumina consisting, for example, in the saponification of glycerides¹ and deacetylation of acetylated sugars^{2,3} and other types of decomposition have been reported in the literature.

LEDERER AND LEDERER⁴ have referred to the decomposition of the picrates of aromatic hydrocarbons as a practical method for their purification and indicated its application to styphnates and trinitrobenzolates^{5,6}.

However, LEDERER *et al.* in their publication⁵ on ambergris have mentioned the decomposition of the picrate of a hydrocarbon obtained from ambreinolide by passing its solution through alumina and describe the styphnate but not its decomposition.

J. Chromatog., 23 (1966) 312-315

Further, LEDERER, MERCIER AND PÉROT⁶, in connection with their studies on the structure of ambreine, describe the purification of 1,2,5,6-tetramethylnaphthalene *via* decomposition of its picrate but not that of its styphnate.

The purification of hydrocarbons by decomposition of their molecular derivatives by passing through a column of alumina seems to have been mentioned first by PLATTNER AND PFAU⁷, who purified azulene and some of its derivatives by chromatographic decomposition of the corresponding picrate and trinitrobenzolate on Brockmann alumina.

The present work describes the systematic application of chromatographic decomposition of the molecular acid derivatives, *viz.* picrates, trinitrobenzolates and styphnates, on basic alumina, to the purification of some representative polycyclic hydrocarbons on a quantitative scale.

The incentive for this work came principally from the difficulties faced in the purification of 1,2,3,4,9,10,11,12-octahydrotriphenylene in connection with our work on a total synthesis of triphenylene⁸. This could only be obtained in a crystalline form, by the decomposition of its picrate on basic alumina.

Materials

The picrates of naphthalene (I), anthracene (II), phenanthrene (III), acenaphthene (IV), 1,2,3,4-tetrahydrophenanthrene (V) and 1,2,3,4,9,10,11,12-octahydrotriphenylene (VI) and the styphnates and trinitrobenzolates of I-V were prepared by heating equimolecular solutions of the hydrocarbons I-VI and picric acid, styphnic acid or trinitrobenzene in benzene, acetic acid and ethanol respectively for 15 min on the water bath with subsequent crystallization at room temperature, except the styphnate of anthracene, which was prepared in benzene solution. They were purified by recrystallization from benzene-petroleum ether mixture, acetic acid and ethanol respectively, with the exception of the picrate of V which was recrystallized from ethanol and of anthracene styphnate, which was best recrystallized from benzene.

Method

Chromatographic decomposition. Weighed quantities of the respective picrates, styphnates or trinitrobenzolates were dissolved in a minimum amount of benzene and allowed to pass over a column of a weighed quantity of basic alumina (Woelm, activity I). The hydrocarbons were eluted by measured quantities of petroleum ether (60-80°). The trinitrobenzolates were applied on the column in a minimum quantity of benzene-petroleum ether (1:2) (60-80°) solution. Special care was taken to use more than a minimum quantity of benzene in order to avoid the presence of trinitrobenzene in the eluates.

The above method was also extended with success to the purification of α - and β -naphthols and α - and β -naphthylamines by decomposing their picrates. These picrates were applied on the column in a minimum quantity of ethyl acetate and eluted with the same solvent.

Results

Tables I to III give the qualitative and quantitative data for the purification and the yields of the purified hydrocarbons finally obtained.

TABLE I

DECOMPOSITION OF PICRATES

In each case 7-8 g of basic alumina was used for preparing the column.

Hydrocarbons	Picrates		Volume of eluent petroleum ether (ml)	Purified hydrocarbons		Yield (%)
	M.p. (°C)	Weight (mg)		M.p. (°C)	Weight (mg)	
(I)	148-149	100	150	79-80	32	91
(II)	139-140	160	150	212-213.5	65	93
(III)	144-145	185	130	99-100	75	92
(IV)	161-162	200	150	94-94.5	76	92
(V)	110-111	100	120	31-32	40	89
(VI)	196-198	100	150	121-122	48	94

TABLE II

DECOMPOSITION OF STYPHNATES

In each case 4-5 g of basic alumina was used for preparing the column.

Hydrocarbons	Styphnates (recrystallized)		Purified hydrocarbons (eluted with 80 ml* of petroleum-ether, 60-80°)		Yield (%)
	M.p. (°C)	Weight (mg)	M.p. (°C)	Weight (mg)	
(I)	162-164	100	79-80	32	94
(II)	180-181	150	211-214	60	95
(III)	142-144	80	98-100	32	94
(IV)	152-154	100	93-94	36.5	96
(V)	136-138	60	31-32	24	94

* In the case of V only 60 ml of eluent was required.

TABLE III

DECOMPOSITION OF TRINITROBENZOLATES

In each case 10 g of basic alumina was employed for each 100 g of the trinitrobenzolate.

Hydrocarbons	Trinitrobenzolates (recrystallized)	Volume of eluent (petroleum ether)	Purified hydrocarbons		Yield (%)
			M.p. (°C)	Weight (mg)	
(I)	148-149	60 ml	79.5-80	35	96
(II)	162-163	60 ml	212-213	42	93
(III)	163-164	80 ml	96-97	43	95
(IV)	164-166	60 ml	93-94	40	95
(V)	128.5-129	80 ml	29-30	44	95

TABLE IV

U.V. ABSORPTION SPECTRA

	Max ($m\mu$)	a (ϵ)	b (ϵ)
(1) <i>Acenaphthene</i>	227	76200	91800
	243	1075	1145
	270	3720	3920
	279	5630	5920
	288.5	6330	6650
	299.5	3940	4100
	305.5	2600	2700
	313	910	955
	320	1340	1365
(2) <i>Anthracene</i>	245	100700	111100
	251.5	181000	197000
	309	1145	1160
	323.5	2680	3120
	339	5070	5320
	356	7300	7750
	374	7170	7620
(3) <i>Phenanthrene</i>	211	31750	32400
	245	48200	49700
	250.5	63800	64300
	273.5	12480	13600
	280.5	9600	10420
	292	11580	12680

The hydrocarbons I to IV used as starting materials were commercial products with melting points 78–80°, 209–212°, 95–98°, 93–94°, and V and VI were intermediates obtained in this laboratory both as coloured oily products. The melting points of the purified hydrocarbons mentioned in the tables are those of products recrystallised in ethanol (I–IV), petroleum ether (60–80°) (V) and benzene (VI).

Table IV, showing the ultraviolet spectra of acenaphthene, anthracene and phenanthrene, both for (a) impure and (b) purified products, gives an idea of the grade of purification obtained by chromatographic decomposition of the picrates of the same.

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Received November 23rd, 1965